



Preparation and Characterization of Organic-Inorganic Hybrid Coating Surface with Gradient Wettability

LIANG ZHOU¹, ZIHING HUANG², YUHONG TAO² and JIANG CHENG^{2,*}

¹Department of Chemical Engineering, Guangdong Industry Technical College, Guangzhou 510300, P.R. China

²School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510640, P.R. China

*Corresponding author: E-mail: cejcheng@scut.edu.cn, zhou.liang@port.ac.uk

Received: 14 June 2014;

Accepted: 9 September 2014;

Published online: 27 April 2015;

AJC-17170

The organic-inorganic hybrid coating surface with gradient wettability of water contact angle from 12.0 to 85.3° was prepared by slowly adding hexamethoxy methyl melamine and subsequently fluoro-contained acrylic polymer into an organic-inorganic hybrid hydrophilic polymer synthesized by tetraethoxysilane (TEOS) and acrylic acid (AA) while the microslide substrate was gradually lifted up from the above mixture. After finally taken out from the solution the coated microslide was then cured in an oven at 220 °C for 90s to form the wettability gradient surface. X-ray photoelectron spectroscopy was employed to characterize the surface chemical composition of the gradient surface. The method overcomes the limitation of restrictive substrate and reactive conditions, providing potential applications in areas such as protein absorption, microfluidics and heat transfer enhancement.

Keywords: Hydrophilic polymer, Gradient wettability, Organic-inorganic hybrid coating surface, Hexamethoxy methyl melamine.

INTRODUCTION

Gradient wettability surfaces¹ have recently received much attention due to their potential applications in cell or protein adhesion/absorption^{2,3}, microfluidics or wetting process⁴⁻⁷ and heat-transfer enhancement in heating/cooling systems^{8,9}. A number of gradient preparation techniques for various substrates were reported¹⁰⁻¹⁴, including self-assembly, ionic exchange and illumination through chemical composition gradient; polymer melting, ionic polymerization and laser-etching method through surface roughness gradient. Most fabrication procedures may need either particular materials (such as silicon wafer substrate or precious metals) or strict reactive conditions. Yu *et al.*¹¹ fabricated a gradient wettability surface by controlling the self-assembled monolayer consisting of a thiol molecule on an expensive gold material surface. Sun *et al.*¹⁴ produced a surface wettability gradient from superhydrophobicity to hydrophobicity by creating surface roughness gradient on a polished silicon wafer with excimer laser.

Herein, we proposed a simple method for fabricating a gradient wettability surface. The contact angles of the coating surface increased continuously from the upper part to lower part along the length of the microslide substrate, which was achieved by slowly adding hexamethoxy methyl melamine and fluoro-contained acrylic polymer orderly into an organic-inorganic hybrid hydrophilic polymer while gradually lifting

the substrate from the mixture. This preparation method is not limited by specified substrates or restrictive reactive conditions, providing a new strategy for preparation of functional wettability gradient surfaces with potential application in the above mentioned areas.

EXPERIMENTAL

Chemicals including tetraethoxysilane, KH-570, ethanol, HCl, azodiisobutyronitrile (AIBN), acrylic acid, hexamethoxy methyl melamine and 2-(perfluoroalkyl)ethyl methacrylate (TM), all are analytical grade, obtained domestically and used as received without further treatment.

Synthesis of organic-inorganic hybrid hydrophilic polymer: Tetraethoxysilane and KH-570 were added into a mixture of ethanol and H₂O, with drops of HCl to regulate pH to 3.5. The molar ratio of both water and ethanol to tetraethoxysilane was 6 % and the dosage of KH-570 was 5 % of tetraethoxysilane. The solution was then stirred at 60 °C for 3 h to form the modified SiO₂ sol.

Ethanol was poured into a reactor fitted with a reflux condenser and an agitator. When the reactor temperature reached 78 °C, the mixture of the above modified SiO₂ sol, acrylic acid and azodiisobutyronitrile was added into the reactor drop-by-drop within 1.5 h. The solution was further kept stirring at 78 °C for 3 h.

Synthesis of fluoro-contained acrylic polymer: Similarly ethanol was filled into a reactor fitted with a reflux condenser and an agitator and the mixture of 2-(perfluoroalkyl) ethyl methacrylate, acrylic acid and azodiisobutyronitrile was added into the reactor drop-by-drop for 1.5 h under stirring and the reaction temperature of 78 °C. The solution was kept stirring at 78 °C for another 3 h.

Preparation of gradient wettability surface: As shown in Fig. 1, a certain amount of the organic-inorganic hybrid hydrophilic polymer was filled into a beaker. The microslide substrate clamped with a deceleration device was immersed in the hydrophilic polymer with its terminal part of 2 cm length under the liquid surface. While the substrate was risen up in a speed of 1mm/min and the hydrophilic polymer kept mild stirring, hexamethoxy methyl melamine was added slowly into the hydrophilic polymer (this process needs around 20 min) and subsequently the fluoro-contained acrylic polymer was slowly added into mixed polymer (this process takes further 10 min). Finally, the substrate was taken out and cured in oven at 220 °C for 90s, to form the wettability gradient coating surface on the microslide substrate.

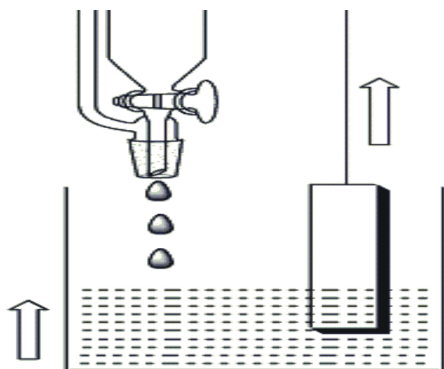


Fig.1. Experimental device for preparing gradient wettability surface

The water contact angles on the coating surface at different positions along the substrate were measured by an OCA15 (Data Physics Instruments Company, Germany) and the volume of water droplets was kept at about 3 μ L. Contact angles values were obtained by averaging five measurement results at the same position on the gradient wettability surface. X-ray photoelectron spectroscopy (XPS) (Vario EL III, Elementary, Germany) was applied to analyze the surface chemical composition of the gradient wettability surface.

RESULTS AND DISCUSSION

Fig. 2 shows the effect of different mass ratios of TEOS/(TEOS + acrylic acid) and different dosages of hexamethoxy methyl melamine on the wettability of coating surface. As shown in Fig. 2 the organic-inorganic hybrid hydrophilic polymer displayed good hydrophilicity (the minimum contact angle of 12°) when the mass ratio of TEOS/(TEOS + acrylic acid) was inferior to 0.3. The contact angles of coating surface gradually increased as hexamethoxy methyl melamine was added constantly into the hydrophilic polymer because the methoxy groups of hexamethoxy methyl melamine can react with hydrophilic groups (-COOH and -Si-OH) of the hydrophilic polymer, leading to the gradient reduction of hydrophilic

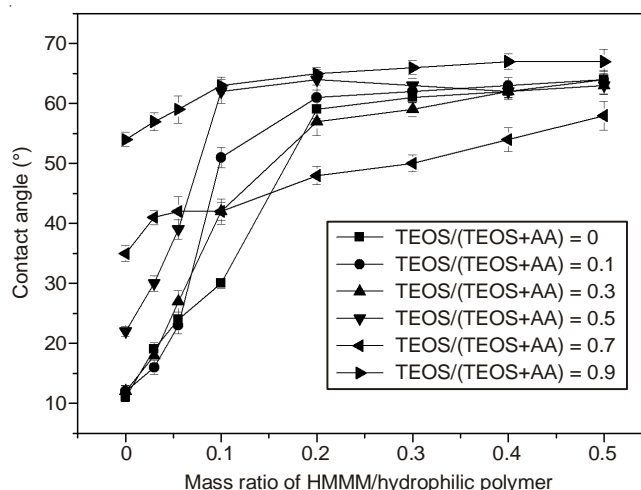


Fig. 2. Effect of TEOS/(TEOS + acrylic acid) ratio and hexamethoxy methyl melamine (HMMM) dosage on wettability

groups (-COOH and -Si-OH) along the coating surface. When the dosage of hexamethoxy methyl melamine was greater than 20 % of the hydrophilic polymer, the contact angles reached about 60.0° and remained almost unchanged with further addition of hexamethoxy methyl melamine.

For further increase the contact angle and enlarge the wettability gradient range after finishing addition of hexamethoxy methyl melamine. The synthesized fluoro-contained acrylic polymer was applied as described above in the experimental section. Fig. 3 shows the effect of dosage of fluoro-contained acrylic polymer on the coating surface wettability. It can be seen that when the dosage of 2-(perfluoroalkyl)ethyl methacrylate was higher than 5 % in the fluoro-contained acrylic polymer and the addition of as-synthesized fluoro-contained acrylic polymer greater than 10 % of the organic-inorganic hybrid hydrophilic polymer the contact angle may reach about 85° and remained approximately stable with further addition of the fluoro-containing acrylic polymer.

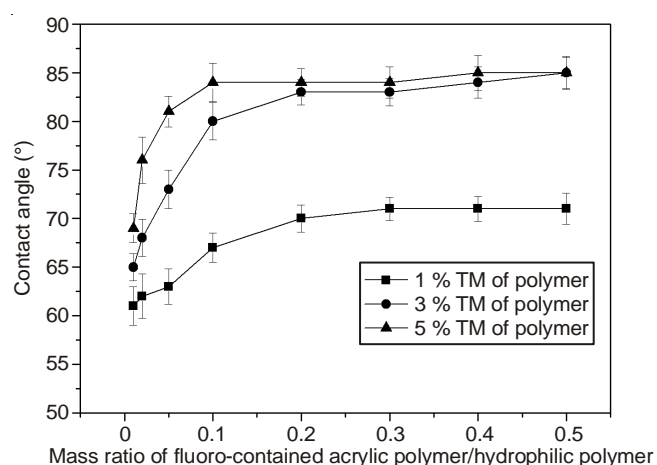


Fig. 3. Effect of dosage of fluoro-contained acrylic polymer on wettability

As described above, the organic-inorganic hybrid hydrophilic polymer was prepared as the mass ratio of TEOS/(TEOS + acrylic acid) was 0.3. While the microslide substrate was lifted up with a speed of 1 mm/min, slowly adding hexamethoxy methyl melamine (the dosage of hexamethoxy methyl melamine

was 20 % of the hydrophilic polymer) into the organic-inorganic hybrid hydrophilic polymer (this process needs 20 min) and then adding fluoro-contained acrylic polymer (the dosage of fluoro-contained acrylic polymer was about 10 % of the hydrophilic polymer as the content of 2-(perfluoroalkyl) ethyl methacrylate was 5 % in the fluoro-contained acrylic polymer) into the hydrophilic polymer (this process takes 10 min). Positions along the latitude of the substrate would correspond directly to polymer with continuously changing surface energy and wettability. As predicted, the as-prepared substrate exhibited a continuous gradient wettability. As shown in Fig. 4, the contact angles changed continuously along the coating surface from 12.0° to 85.3° in about 2 cm length of the microslide substrate.



Fig. 4. Water contact angles along the coating surface

Fig. 5 shows the XPS C1s core level spectra of the gradient wettability coating surface along the substrate. The spectra were resolved into five Gaussian curve-fitted peaks: hydrocarbon (-CH_n, n=0-3) around 285.0 eV, -COC=O around 286.4 eV, -C=O around 288.6 eV, -CF₂- around 292.0 eV and -CF₃ around 294.0 eV, from low to high binding energy.

Table-1 gives the elemental contents with points "a-e" on the gradient wettability coating surface, whose contact angle corresponds to 12.0°, 30.1°, 61.2°, 70.4°, 81.6°, respectively. As shown in Table-1, the elements vary much along the coating surface. Elements of silicon, oxygen and carbon were detected at point "a" before addition of hexamethoxy methyl melamine. With adding hexamethoxy methyl melamine into the organic-inorganic hybrid hydrophilic polymer, element of nitrogen increases continuously from 0 to 1.99 % and then 4.65 % corresponding to the points "a" to "c", resulting in the increased contact angle on the coating surface. When the fluoro-contained acrylic polymer was subsequently dropped into the mixture of hydrophilic polymer and hexamethoxy methyl melamine, the element of fluorine increases continuously from 0-8.84 to 13.79 %, which accounts for the contact angle further increasing from "c" to "e" point.

TABLE-1
ELEMENTAL CONTENT ALONG THE SUBSTRATE

Elemental content (%)	a(12.0°)	b(30.1°)	c(61.2°)	d(70.4°)	e(81.6°)
F	0	0	0	8.84	13.79
O	41.86	33.8	36.61	32.10	30.41
N	0	1.99	4.65	2.81	2.85
C	42.20	59.40	49.14	53.86	52.13
Si	15.95	4.73	9.60	2.18	0.82

TABLE-2
PEAK AREA OF XPS C1s CORE LEVEL SPECTRA OF THE GRADIENT FILM ALONG THE SUBSTRATE

Points	S _{-CH_n(n=0-3)}	S _{-COC=O}	S _{-C=O}	S _{-CF₂}	S _{-CF₃}	S	S _{-COC=O} /S _{-C=O}	S _{-CF₂-CF₃} /S
a(12.0°)	36537	1370	13632	-	-	-	0.1005	-
b(30.1°)	43749	7013	14386	-	-	-	0.4875	-
c(61.2°)	37209	10899	13555	0	0	61663	0.8046	0
d(70.4°)	37145	11143	16463	1440	7730	73921	-	0.124
e(81.6°)	33660	9311	15147	1908	11558	71584	-	0.188

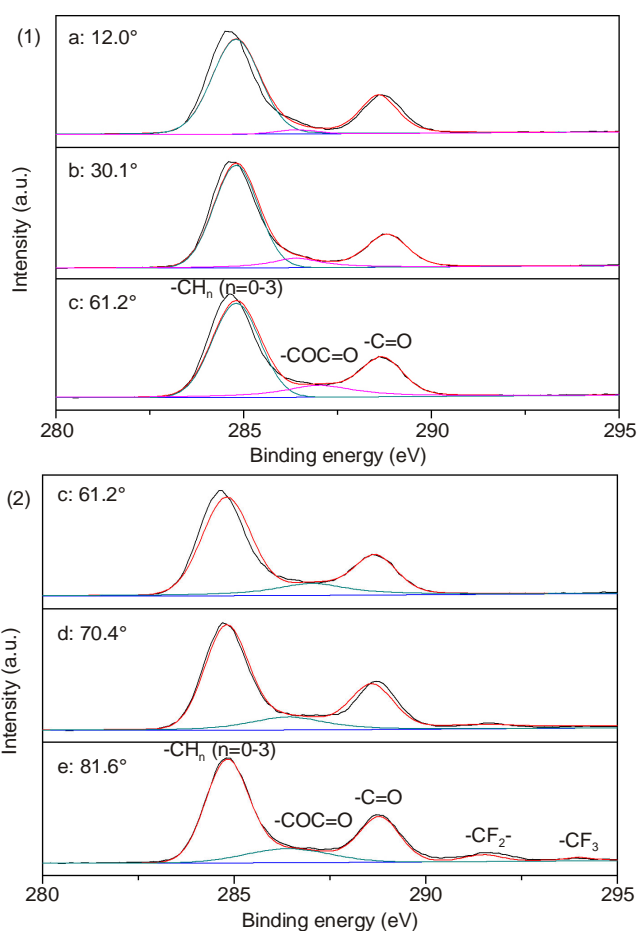


Fig. 5. XPS C1s core level spectra of the coating surfaces with gradient wettability along the substrate: with (1) addition of hexamethoxy methyl melamine and (2) addition of fluoro-contained acrylic polymer

The peak areas of XPS C1s core level spectra were further demonstrated in Table-2. The area ratio of S_{-COC=O}/S_{-C=O} gradually increases from point "a" to "c" as hexamethoxy methyl melamine was added into the hydrophilic polymer. This is because the number of -COC=O groups increases continuously as a result of polycondensation of -COOH or -Si-OH groups contained in hydrophilic polymer with the methoxy group of hexamethoxy methyl melamine. Then the peak areas of -CF₂- and -CF₃ and the ratio of S_{-CF₂-CF₃}/S (S represents for the integral area of all characteristic peaks) increase with addition of the fluoro-contained acrylic polymer, leading to the further increase of contact angle from point "c" to "e" gradually.

For testing the water resistant property and thermal stability of the prepared gradient wettability coating surface, the coated microslide substrate was immersed in a water bath at 80 °C for 2 h. A comparison between the contact angle of different positions on the microslide after and before immersion in

hot water was shown in Fig. 6. The result demonstrates that changes of contact angle (most within 10°) occurred near the hydrophilic section of the substrate, which may be attributed to the insufficiency of curing effect during the initial stage of hexamethoxy methyl melamine addition, indicating the water durability of the prepared gradient coating surface needs to be further improved especially with the more hydrophilic side in the future study.

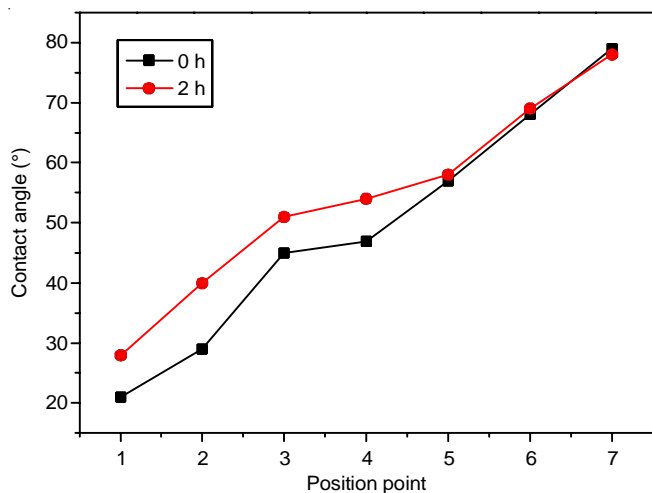


Fig. 6. Comparison of contact angle before and after immersion in hot water (80°C) for 2 h

Conclusion

In summary, we have developed a simple and novel method to fabricate a coating surface with gradient wettability from 12.0° to 85.3° . It was prepared by adding hexamethoxy methyl melamine into an organic-inorganic hybrid hydrophilic polymer to gradually reduce the hydrophilic groups and subsequently the fluoro-contained acrylic polymer with low surface energy into the above hydrophilic polymer to further enlarge

the contact angle range. Both would gradually increase the contact angles along the coating surface while lifting slowly the coated substrate from the mixture. The X-ray photoelectron spectroscopy measurements were used to analyze the chemical compositions change along the coating surface and the formation of the wettability gradient. This method provides a new strategy for preparation of functional wettability gradient surfaces with potential engineering application, but needs further improvement in water durability especially with the more hydrophilic side in future study.

ACKNOWLEDGEMENTS

The authors thank the financial support of Guangdong Natural Science Foundation (S2012010010417).

REFERENCES

1. X.F. Li, H.J. Dai, S.X. Tan, X.Y. Zhang, H.Y. Liu, Y.X. Wang, N. Zhao and J. Xu, *J. Colloid Interf. Sci.*, **340**, 93 (2009).
2. K. Loos, S.B. Kennedy, N. Eidelman, Y. Tai, M. Zharnikov, E.J. Amis, A. Ulman and R.A. Gross, *Langmuir*, **21**, 5237 (2005).
3. H. Elwing, S. Welin, A. Askendahl and I. Lundström, *J. Colloid Interf. Sci.*, **123**, 306 (1988).
4. K. Ichimura, S.K. Oh and M. Nakagawa, *Science*, **288**, 1624 (2000).
5. B.S. Gallardo, V.K. Gupta, F.D. Eagerton, L.I. Jong, V.S. Craig, R.R. Shah and N.L. Abbott, *Science*, **283**, 57 (1999).
6. S. Daniel, M.K. Chaudhury and J.C. Chen, *Science*, **291**, 633 (2001).
7. X. Ye, M. Zhou, D. Jiang, J. Li and L. Cai, *J. Central South Univ. Technol.*, **17**, 554 (2010).
8. T.S. Leu, H.W. Lin and T.H. Wu, *Mod. Phys. Lett. B*, **24**, 1381 (2010).
9. Q. Liao, Y.B. Gu, X. Zhu, H. Wang and M.D. Xin, *Enh. Heat. Transfer*, **14**, 243 (2007).
10. E. Paul, T.P. Beebe, K.J. Uram and J.T. Yates, *J. Am. Chem. Soc.*, **114**, 1949 (1992).
11. X. Yu, Z.Q. Wang, Y.G. Jiang and X. Zhang, *Langmuir*, **22**, 4483 (2006).
12. Y. Ito, M. Heydari, A. Hashimoto, T. Konno, A. Hirasawa, S. Hori, K. Kurita and A. Nakajima, *Langmuir*, **23**, 1845 (2007).
13. J.L. Zhang, L.J. Xue and Y.C. Han, *Langmuir*, **21**, 5 (2005).
14. C. Sun, X.W. Zhao, Y.H. Han and Z.Z. Gu, *Thin Solid Films*, **516**, 4059 (2008).